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<b>(54) Title:</b> PROCESS FOR PURIFICATION OF AROMATIC POLYCARBOXYLIC ACIDS  <b>(57) Abstract</b>  The present invention provides a process for purifying crude aromatic polycarboxylic acids having one or more condensed rings with two or more carboxylic acid groups on the aromatic ring or rings. The process uses solvents comprising a mixture of a major solvent and a co-solvent, wherein the major solvent is selected from a group consisting of a monocyclic compound containing two hetero-atoms, an alkylamine compound and mixtures thereof, and the co-solvent is selected from a group consisting of water, an alcohol, and mixtures thereof.		

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## PROCESS FOR PURIFICATION OF AROMATIC POLYCARBOXYLIC ACIDS

### FIELD OF INVENTION

This invention relates to a process for purifying aromatic polycarboxylic acids.

### 5 BACKGROUND OF THE INVENTION

The purification process in the present invention relates to purifications of aromatic polycarboxylic acids having one or more condensed aromatic rings and two or more carboxylic acid groups. The aromatic polycarboxylic acids include, but are not necessarily limited to terephthalic acid, isophthalic acid and trimellitic acid; 2,6-  
10 naphthlene dicarboxylic acid, 2,7-naphthalene dicarboxylic acids, and 2,3,6-anthracene tricarboxylic acid.

Terephthalic acid, an important starting material for polyesters, has a large commercial market. Terephthalic acid is difficult to purify due to its low solubility in most solvents, its high boiling point, and because its physical and chemical properties  
15 are similar to those of the impurities present in crude terephthalic acid (CTA).

Polymer-grade terephthalic acid, called purified terephthalic acid, (PTA) must meet stringent specifications to be suitable for the production of polyesters such as polyethylene terephthalate (PET) and polybutene terephthalate (PBT). The presence of its major impurities, p-toluic acid, benzoic acid, and 4-carboxybenzaldehyde (4-  
20 CBA), even in minute amounts, will adversely affect the quality of the polymer products. P-toluic acid and benzoic acid act as polymerization terminators. 4-CBA causes undesirable coloring of the polymer products. Commercial PTA's have maximum 25 ppm of residual 4-CBA and 150 ppm of p-toluic acid. Residual benzoic acid is generally low and not specified.

25 The PTA manufacturing process has two major sections: an oxidation reaction section and a purification section. The oxidation reaction section, usually a liquid phase oxidation reaction of paraxylene (PX), is for the production of CTA. CTA then is introduced to the purification section for removal of impurities. CTA is also present as a major component in some intermediate streams of the dimethyl terephthalate  
30 (DMT) production processes.

With slight variations, the purification section of conventional processes removes 4-CBA from terephthalic acid by chemically converting 4-CBA into p-toluic acid

through hydrogenation reaction using charcoal supported noble metals, such as platinum, palladium, and so on, as the catalysts. P-toluic acid is removed by recrystallizing terephthalic acid from water at elevated temperatures and pressures. An alternative is continuing further oxidation of 4-CBA to terephthalic acid.

- 5       The purification methods, by hydrogenation or by oxidation, although efficient, can only handle relatively small initial amount of 4-CBA present in CTA. 4-CBA, the principal impurity present in CTA, is limited to less than 1.0 wt%, preferably less than 0.5 wt%, to avoid overloading the purification section of the process.

10       In order to reduce the amount of initial impurities introduced into the purification section, the oxidation reaction section equipment has to run at higher severity. Alternatively, additional processing steps are added after the oxidation reaction section. Examples of such additional steps are secondary oxidation step and re-slurrying CTA in fresh acetic acid. Higher severity in the oxidation reaction section increases the combustions of PX feedstock, the overall yield of the desired product and  
15       production efficiency are reduced. Using acetic acid as solvent and operating under severe condition require expensive corrosion resistant metals, such as titanium, for the PX oxidation reactor and some other parts of the process. This requirement increases initial capital investment significantly.

20       CTA can be purified by crystallization in organic solvents. Examples are N,N-dimethylacetamide, or N,N-dimethylformamide, or their mixtures with water or methanol (U.S. Patent 2,811,548); pyridine with isopropylamine, recrystallizing in ethylene glycol, and acidifying in acid water (U.S. patent 2,829,160) N-formyl morpholine, or N-formyl piperidine (U.S. Patent 2,849,483); and ammonia with methanol and acetone (U.S. Patent 2,862,963). The organic solvents, as disclosed,  
25       have several disadvantages. Some of them are unable to produce PTA. Others are either chemically or thermally unstable. Some tend to produce additional products by reacting with terephthalic acid itself. It is also difficult to separate the residual solvent included in the crystals of the product.

30       The thermally more stable and chemically much less reactive solvents such as acetic acid, acetic anhydride and water have low terephthalic acid solubility. Separation between terephthalic acid and 4-CBA in these solvents is not good enough.

Consequently, additional hydrogenation is required to convert 4-CBA to p-toluic acid, which is removed by recrystallization in water.

The manufacturing processes of isophthalic acid, phthalic acid, benzenetricarboxylic acids, aromatic polycarboxylic acids with two condensed rings, such as naphthalene dicarboxylic acids (NDA), are similar to the PTA process. Similar purification procedures are required.

### SUMMARY OF THE INVENTION

The invention relates to a process for purifying a crude aromatic polycarboxylic acid having one or more condensed rings. The process comprising: dissolving the crude aromatic polycarboxylic acid in a solvent comprising a substance selected from the group consisting of a major solvent and a mixture of a major solvent and a co-solvent wherein said co-solvent is selected from the group consisting of water, an acid solvent, an oxygen-containing solvent, and mixtures thereof, wherein the proportion of said major solvent to said co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said solvent is used in an amount from 0.1 to 100 times by weight of the amount of said crude aromatic polycarboxylic acid; conducting a purification process; and filtering to obtain a high purity aromatic polycarboxylic acid.

The invention also relates to a process for purifying a crude aromatic polycarboxylic acid having one or three condensed rings. The process comprises: dissolving the crude aromatic polycarboxylic acid in a solvent comprising a substance selected from the group consisting of a major solvent and a mixture of a major solvent and a co-solvents, wherein the co-solvent is selected from the group consisting of an alcohol, water, an acid solvent, an oxygen-containing solvent, and mixtures thereof, wherein the proportion of the major solvent to the co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said solvent is used in an amount from 0.1 to 100 times by weight of the amount of the crude aromatic polycarboxylic acid; conducting a purification process; and filtering.

The invention relates to a process for purifying a crude aromatic polycarboxylic acid having two condensed rings. The process comprises: dissolving the crude aromatic polycarboxylic acid in a solvent comprising a substance selected from the group consisting of an N,X-monocyclic compound, an alkylamine compound, a

mixture comprising a material selected from the group consisting of the N,X-monocyclic compound and the alkylamine compound, and a co-solvent wherein the co-solvent is selected from the group consisting of an alcohol, water, an acid solvent, an oxygen-containing solvent, and mixtures thereof, wherein the proportion of said major solvent to the co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said solvent is used in an amount from 0.1 to 100 times by weight of the amount of said crude aromatic polycarboxylic acid; conducting a purification process to precipitate the aromatic polycarboxylic acid wherein the composition of the solvent is changed by removing a portion of the solvent; and filtering to obtain a high purity aromatic polycarboxylic acid product having two condensed rings.

#### **DETAILED DESCRIPTION OF THE INVENTION**

##### **Crude Aromatic Polycarboxylic Acids**

The aromatic polycarboxylic acids that are suitable for purification in accordance with the present invention are aromatic acids having one or more condensed rings, and two or more carboxylic acid group substituents are at the aromatic ring or rings. One-ring aromatic dicarboxylic acids include, but are not necessarily limited to terephthalic acid, isophthalic acid, orthophthalic acid, trimellitic acid, hemimellitic acid, trimesic acid, pyromellitic acid, and mellitic acid. Two-ring aromatic polycarboxylic acids include, but are not necessarily limited to 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 1,7-naphthalene dicarboxylic acid, 1,8-naphthalene dicarboxylic acid, 2,3,6-naphthalene tricarboxylic acid, 1,4,5,8-naphthalene tetracarboxylic acid, and 2,3,6,7-naphthalene tetracarboxylic acid. The three-condensing ring aromatic polycarboxylic acids include but are not necessarily limited to 2,6-anthracene dicarboxylic acid, 2,7-anthracene dicarboxylic acid, 2,8-anthracene dicarboxylic acid, 2,9-anthracene dicarboxylic acid, 1,9-anthracene dicarboxylic acid, 2,3,6-anthracene tricarboxylic acid, 1,4,5,8-anthracene tetracarboxylic acid, and 6,7-anthracene tetracarboxylic acid.

Most crude aromatic dicarboxylic acids (CAPA) are obtained by oxidation processes of poly-substituted aromatic compounds with air or oxygen enriched air. For example, oxidation of PX produces terephthalic acid. The oxidation process is commonly carried out in a solvent, in the presence of a catalyst containing heavy metals such as cobalt, manganese, or their mixture, and in the presence of a promoter

such as bromine. Acetic acid is the commonly used solvent. Crude aromatic polycarboxylic acid is the major product from oxidation.

Another source of crude aromatic polycarboxylic acid is from the intermediate-stream product in an aromatic polycarboxylic ester production process. For example, CTA can be obtained from the oxidizer effluent during the production of DMT; crude 2,6-NDA can be recovered from the oxidizer effluent during the production of dimethyl 2,6-naphthalene dicarboxylate (NDC). The impurity content of CTA obtained from DMT process may be as high as 30 wt%. It will cause overloading problem purification processes by oxidation or hydrogenation as discussed previously. However, the present invention is capable to purify such a kind of intermediate product to their polymer-grade specifications.

The major impurities present in some crude aromatic polycarboxylic acids (CAPA) are listed below:

	Process	Impurities
Terephthalic acid	Oxidation	4-CBA, p-toluic acid, benzoic acid
Isophthalic acid	Oxidation	3-CBA, m-toluic acid, benzoic acid
Orthophthalic acid	Oxidation	2-CBA, o-toluic acid, benzoic acid
2,6-NDA	Oxidation	Trimellitic acid, bromo-2,6-NDA, 2-naphthoic acid, 2-formyl-6-naphthoic acid
Terephthalic acid	Esterification	4-CBA, p-toluic acid, benzoic acid, monomethyl terephthalate, dimethyl terephthalic acid, methyl p-toluate, dimethyl terephthalate, methylbenzoate
2,6-NDA	Esterification	Trimellitic acid, bromo-2,6-NDA, 2-naphthoic acid, 2-formyl-6-naphthoic acid, 2,6-NDC, 2-formyl-6-naphthoic acid, esters of trimellitic acid

15

#### Solvents

The following lists the solvents that can be used in this invention. These solvents used may include a single solvent, a mixture, or an admixture of solvents that can be totally miscible (one phase) or partially immiscible (two phases). The solvents are

categorized into major solvents, co-solvents, and acid solvents. A mixed solvent comprises a major solvent, a co-solvent, and an acid solvent.

### Major Solvents

5 Without limiting the scope of the invention, it is believed that a major solvent dissolves aromatic polycarboxylic acids and most impurities by forming weakly bonded complexes. A major solvent of the present invention comprises a substance selected from the group consisting of an N,X-monocyclic compound, an alkylamine compound and mixtures thereof.

### 10 N,X-Monocyclic Compound

An N,X-monocyclic compound in the present invention comprises a mono-heterocyclic compound containing 3 to 8 atoms in the ring with a nitrogen(N) and an hetero-atom(X), such as oxygen, sulfur, or another nitrogen, as the hetero-atoms. The nitrogen atoms may have three or five valences. The N,X monocyclic compound  
15 include but are not necessarily limited to compounds having hetero-atoms and carbon-atom at different positions in the ring, saturated and unsaturated compounds with one or more hydrogen atoms that may be substituted by an alkyl, aryl, or acyl group, and ammonium salts derived from such compounds.

An N,X-monocyclic compound includes but is not necessarily limited to a parent  
20 compound, a saturated or unsaturated ring with hetero-atom at possible ring positions, such as oxazocines, oxazepines, oxazines, oxazoles, isoxazoles, oxadiazetes, oxazirines, thiozocines, thiazepines, thiazines, thiazoles, isothiazoles, thiazetes, thiazirines, diazocines, diazepines, pyrazines, pyridazines, pyrimidines, imidazoles, pyrazoles, diazetes, and diazirines. If a compound is a solid or gas under normal  
25 condition, its aqueous solution from 0.0001wt% to saturation is used.

The N,X-monocyclic compound can be used either alone or as a mixture of two or more N,X-monocyclics. A preferred N,X-monocyclic compound for the present invention comprises a saturated oxazine. The commonly used or adopted name of a saturated oxazine is morpholine, CAS Registry Number 110-91-8. A morpholine  
30 compound in this invention is selected from the group consisting of morpholine, substituted morpholines, morpholine derivatives, and mixtures thereof. Examples of a morpholine compound are morpholine, N-methylmorpholine, N-ethylmorpholine, N-



propylmorpholine, N-isopropylmorpholine, N-methylmorpholine oxide, N-phenylmorpholine, 4-morpholinepropionitrile, 1-morpholine-1-cyclohexene, piperazine, N-methylpiperazine, 2-methylpiperazine, N,N-dimethylpiperazine, 1,4-diazabicyclo[2.2.2]octane (CAS Registry Number 280-57-9), 1,8-diazabicyclo  
5 [5.4.0]undec-7-ene (CAS Registry Number 6674-22-2) and 1,4-diazabicyclo[2.2.2]octane.

#### Alkylamine Compound

An alkylamine compound in this invention includes but is not limited to aliphatic amine, alicyclic amines, ammonium salts derived from these aliphatic and alicyclic  
10 amines.

Aliphatic amines include but are not limited to methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, n-propylamine, di-n-propylamine, tri-n-propylamine, isopropylamine, diisopropylamine, triisopropylamine, cyclohexylamine, C<sub>4</sub> to C<sub>8</sub> aliphatic amines, ethylenediamine, N-methylethylenediamine,  
15 N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N,N'-trimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, N-methyl-1,2-diaminopropane, N-methyl-1,3-diaminopropane, N,N-dimethyl-1,2-diaminopropane, N,N-dimethyl-1,3-diaminopropane, N,N,N'-trimethyl-1,2-diaminopropane, N,N,N'-trimethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,2-diaminopropane, N,N,N',N'-tetramethyl-  
20 1,3-diaminopropane, monoethanolamine, diethanolamine, triethanolamine, and glycine.

Alicyclic amines include but are not limited to pyrrolidine, 1-methyl-pyrrolidine, piperidine, N-methylpiperidine, hexamethyleneimine, and N-methyl hexamethyleneimine. Aliphatic amines having up to 15 carbon atoms are preferred.  
25 Triethylamine and triethanolamine are the most preferred alkylamine compounds. The alkylamine compounds may be used alone or as a mixture of two or more alkylamine compounds thereof. If a compound is in a solid or gaseous form under normal conditions, its aqueous solution from 0.0001wt% to saturation will be used.

#### Co-Solvent

30 The co-solvents suitable for the present invention are water, alcohols and mixtures thereof. Oxygen-containing solvents may be used with a co-solvent or a mixture of co-solvents to enhance further selectivity for product recovery or impurity removal.

Co-solvents also may be used with an acid solvent and/or major solvent to remove residual impurities in the inclusion of the precipitated crystals of the aromatic polycarboxylic acid.

#### Water

5 Water does not react with crude aromatic polycarboxylic acids and their impurities under the operating conditions in the present invention. Using water as the co-solvent enhances the selectivity for product recovery, impurity removal, and reduces the overall cost of solvent used in the invented process to dissolve crude aromatic polycarboxylic acids.

#### Alcohol

10 An alcohol, as a co-solvent, comprises a substance selected from the groups consisting of aliphatic monohydric alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-amyl alcohol, isoamyl alcohol, sec-amyl alcohol, tert-amly alcohol, neopentyl alcohol, 15 hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, and decyl alcohol; alicyclic monohydric alcohols such as cyclopentyl alcohol and cyclohexyl alcohol; aliphatic straight-chain diols such as ethylene glycol, diethylene glycol, glycerol, 1,2-propylene glycol, and 1,3-propylene glycol; alicyclic diols such as 1,2-cyclopentanediol, 1,3-cyclopentanediol, 1,2-cyclohexanediol, 1,3 cyclohexanediol, 1,4-cyclohexanediol; and 20 aliphatic polyols such as glycerol and pentaerythritol. Aliphatic monohydric alcohols having 3 or less carbon atoms and diols having 3 or less carbon atoms, are preferred. Alcohols can be used either alone or as a mixture of two or more alcohols thereof.

#### Oxygen-containing solvents

In addition to water and alcohol, other oxygen-containing solvents may also be 25 used with water, alcohol, and a water and alcohol mixture to further enhance the selectivity of product recovery and impurities removal. The oxygen-containing solvents include but are not necessarily limited to ketones, ethers, aldehydes, glycols, and alicyclic compounds such as furan, dihydrofuran, tetrahydrofuran, tetrahydropyran, 2-methyl cyclopentanone, cyclopentanone, cyclohexanone, 30 cyclohexanol, 2-methyl tetrahydrofuran, 3-methyl tetrahydrofuran, gamma-butyrolactone, and gamma-valerolactone. The oxygen-containing solvents may be used alone or as a mixture of two or more thereof.

### Acid Solvent

An acid solvent includes but is not necessarily limited to aliphatic carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, glycolic acid, lactic acid, malic acid, tartaric acid, mesotartaric acid, citric acid, monochloroacetic acid, 5 monobromoacetic acid, trifluoroacetic acid, and trichloroacetic acid; and inorganic acids such as nitric acid, hydrochloric acid, hydrogen bromide, hydrogen iodide, sulfuric acid, phosphoric acid, and perchloric acid; and mixtures thereof. If an acid is a solid or gas under normal operating conditions, its aqueous solution from 0.0001wt% to saturation is used in.

10 These acid solvents may be used alone or as a mixture of two or more thereof provided they are chemically compatible. Those with ordinary skills in the art would recognize and appreciate that, for example, concentrated sulfuric acid should not be used with hydrogen iodide. The acid solvent may be used as is or in the form of an aqueous solution. An aliphatic carboxylic acid having up to 15 carbon atoms is 15 preferred. The amount of an acid solvent used is in the amount from 0.01 to 100 times, preferably from about 0.2 to 10 times, in molar ratio, to the amount of crude acid present in the solution. The acid solvent includes a mixture of the acid with a co-solvent, in a range from about 0 wt% to about 100 wt%, preferably in a ratio from about 50 wt% to about 99 wt%.

### 20 Mixed Solvent

A mixed solvent comprises a mixture selected from the group consisting of a major solvent and a co-solvent, a co-solvent and an acid solvent, a major solvent and an acid solvent, or a major solvent, a co-solvent and an acid solvent, and mixtures that contain oxygen-containing solvents. The mixed solvent comprises a major solvent from 0.1 25 wt% to 99.9 wt%, a co-solvent from 0.1 wt% to 99.9 wt%, an acid solvent from 0 wt% to 99.9 wt%, and an oxygen-containing compound from 0 wt% to about 85wt%.

The proportion of the N,X-monocyclic compound to water or alcohol is in the range of from 1:1000 to 1000 :1 by weight, preferably from 25:75 to 95:5 by weight. The proportion of the alkylamine compound to water or alcohol in the mixed solvent is 30 in the range of from 1:1000 to 1000:1 by weight, preferably from 25:75 to 95:5 by weight.

The total amount of the major or mixed solvent to be used in this invented process is not specifically limited as long as it is sufficient to dissolve the crude aromatic polycarboxylic acid to minimize losses of CAPA. The amount usually varies depending on the composition and concentration of water or alcohol present in the  
5 N,X-monocyclic compound or alkylamine compound, and the temperature at which the crude aromatic polycarboxylic acid is dissolved. The amount of a major solvent or a mixed solvent is used in the range of from 0.1 to 100 times by weight, preferably from 1 to 50 times by weight, to the amount of the crude aromatic polycarboxylic acid. If the amount of solvent used is below the lower limit specified above, purification  
10 effect may be insufficient. If the amount exceeds the upper limit specified above, while technically feasible and included in this invention, the process becomes less economical.

A solution is a mixture of CAPA dissolving in a major solvent, a major solvent and a co-solvent, or a mixed solvent. After aromatic polycarboxylic acid is precipitated  
15 from the solution, the remaining solution is called a mother liquor.

Most major solvents do not react with oxygen in air under the operating conditions of this invention. Some solvents do react and cause a gradual change of solvent color. Under this circumstance, the process will be preferably operated under low oxygen environment or non-oxidizing atmosphere in a closed system and/or by purging with a  
20 non-oxidizing or inert gas or other suitable methods. Examples of such non-oxidizing or inert gases are N<sub>2</sub>, CO<sub>2</sub>, CO, Ar, He, and H<sub>2</sub>. N<sub>2</sub> and CO<sub>2</sub> are preferred.

A co-solvent is used to increase CAPA solubility or to decrease the solubility of the aromatic polycarboxylic acid to enhance product recovery. For instance, pure N-methyl morpholine oxide has about 15% solubility for terephthalic acid at room  
25 temperature. This solubility is too high for economic recovery of PTA. Adding a suitable amount of water to the solution reduces the solubility and enhances PTA product recovery.

A mixed solvent may be a miscible or immiscible mixture of its components. Therefore, the mixed solvent may be in a single phase or multiple phases. In multiple  
30 phases, the solubilities of crude aromatic carboxylic acids and impurities in different phases may be different. A proper choice of solvent in different phase allows us to take advantage of liquid-liquid extraction method to separate the impurities.

### Solution Pretreatment

The invented purification process precipitates pure aromatic polycarboxylic acids from solutions while keeping as much impurities in the solution as possible. But, CAPA may contain insolubles, color substances, or impurities that can be easily separated by a pretreatment of the solution. The following lists the optional pretreatment methods that can be used individually or in any combination to remove such substances.

- Filtration, centrifugation, sedimentation, magnetic separation, and evaporation.
- Treatment with an activated carbon or other suitable adsorbents by: (1) a batch-wise method in which a predetermined amount of activated carbon or other adsorbent is added to the solution, and the resulting mixture is stirred, with or without heating, and then filtered; or (2) a counter current or co-current continuous method in which the solution is passed through a column packed with activated carbon or other adsorbents.
- Liquid-liquid extraction by choosing solvents that are not immiscible.

### Purification Processes

After a CAPA is dissolved in a solvent, a purification process useful for the present invention comprises one or more of the following five processes. The choice depends on the CAPA to be purified, the solvent selected, and the operating conditions. Details are set forth throughout the specifications. The processes can be used for one to fifty times. The purification processes may be carried out in a non-oxidizing atmosphere. Typical gases are N<sub>2</sub>, CO<sub>2</sub>, CO, Ar, He, H<sub>2</sub>, and mixtures thereof.

Following CAPA dissolution is a purification process selected from the five processed described below. The basic hypotheses of this invention are described herein and they are believed to be true, they are used only to illustrate and demonstrate the invention. The hypotheses are not intended to limit the scopes or inventiveness of this invention.

#### Process 1.

- (a) Changing the composition of the solvent used to dissolve the crude aromatic polycarboxylic acid by removing lower-boiling components in the mixed solvent by flashing under reduced process pressure, by evaporating at constant or variant

temperatures, by distillation, or by adding more co-solvent, to precipitate the solid formed between aromatic polycarboxylic acid and the major solvent.

(b) Separating the precipitated solid followed by treating the separated solid with an acid solvent to obtain a purified aromatic polycarboxylic acid.

5    Process 2.

(a) The same process as 1 (a) is used to precipitate a solid.

(b) Separating the precipitated solid followed by heating the separated solid to a higher temperature, with or without purging with a non-oxidizing or inert gas such as N<sub>2</sub>, CO<sub>2</sub>, CO, He, Ar, H<sub>2</sub>, and mixtures thereof, to decompose the solid  
10        to obtain a purified aromatic polycarboxylic acid.

Process 3.

(a) A crude aromatic polycarboxylic acid is dissolved in a solvent at elevated temperature. The solution is cooled to a lower temperature to precipitate the solid  
15        formed between aromatic polycarboxylic acid and the major solvent.

(b) The solid is separated and then treated with an acid solvent to obtain a purified aromatic polycarboxylic acid.

Process 4.

(a) The same process as 3 (a) is used to precipitate a solid.

(b) The solid obtained is separated and then heated to a higher temperature, with  
20        or without purging with a non-oxidizing or inert gas, such as N<sub>2</sub>, CO<sub>2</sub>, CO, He, Ar, H<sub>2</sub>, and mixtures thereof, to decompose the solid to obtain a purified aromatic polycarboxylic acid.

Process 5.

25        An acid solvent is added to the solution containing the crude aromatic polycarboxylic acid, at constant or variant temperature, to precipitate a purified aromatic carboxylic acid from the solution.

In Process 1 and Process 2, the control and change of the solvent composition depend on the major solvent and co-solvent selected for a particular aromatic  
30        polycarboxylic acid and the desired process conditions. Absolute and relative solubilities of the aromatic polycarboxylic acid to be purified and the impurities present are important. At lower temperatures, around 25°C, the solubilities of aromatic

polycarboxylic acids are generally low in most major solvents or co-solvents. At the lower temperatures, it was unexpectedly discovered that the solubilities of aromatic polycarboxylic acids vary significantly with the composition of the mixture. Most solubilities are negligible in a pure major solvent, increase with the addition of a co-solvent, reach to a maximum, and then gradually decrease to negligible again in a pure co-solvent composition. However, some major solvents were found to have significant solubilities for aromatic polycarboxylic acids at room temperature, and gradually decrease with increasing amounts of co-solvent in the compositions.

Impurity solubilities also vary with co-solvent compositions. Generally, their solubility patterns were found to be similar to, but in a significantly higher absolute level than, aromatic polycarboxylic acid solubilities in a range of compositions.

Higher-boiling components may leave together with lower-boiling components in Process 1 and Process 2. The total amount of solvent removed from the mixed solvent is from 0.1 to 100 wt% of its original amount presented in the mixed solvent, preferably from 50 to 95 wt%. In the case of adding more co-solvent as part of the purification process, the added amount may change the final co-solvent composition from 0.01 to 99.9 wt%, preferably from 20 to 75 wt%. The temperature of solution is from -100 to 350°C, preferably -30 to 180°C; the pressure is in a range of 1 kPa (absolute) to 10MPa (absolute), preferably 20 kPa (absolute) to 200 kPa atmosphere.

In Process 3 and Process 4 above, a crude aromatic polycarboxylic acid is precipitated from solution by cooling. The dissolving temperature may be in the range from -100°C to 350°C, preferably from -80°C to 170°C. The temperature may be cooled to the range from -100 to 150°C, preferably from 25°C to 100°C, more preferably from 40°C to 60°C.

In Process 5, an acid solvent is added to the solution to precipitate purified aromatic polycarboxylic acid while keeping most of impurities in solution. The amount of acid solvent used may be from 0.01 to 100 times, preferably, 0.2 to 30 times, in molar ratio, to the number of moles of crude aromatic polycarboxylic acid present. The operating temperature may vary from -100°C to 350°C, preferably from 25°C to 180°C. This process may be used for 1 to 100 times, preferably, 1 to 3 times.

The solids precipitated by Process 1 and Process 3 are treated by adding a predetermined amount of an acid solvent to the solids. The resulting admixture is

stirred at a temperature from -100 to 350°C, preferably from 25°C to 180°C, for a period of 0 to 10 hours, preferably from 0 to 2 hours. The purified aromatic polycarboxylic acid is recovered subsequently from the mixture. The amount of acid solvent used may be from 0.01 to 100 times by mole, preferably, 0.2 to 10 times by mole, to the amount of crude aromatic polycarboxylic acid. This process may be used for 1 to 100 times, preferably 1 to 3 times.

In Process 2 and Process 4, the exact temperature used to decompose the solids to obtain a purified aromatic polycarboxylic acid is not specifically limited as long as it is sufficient for the decomposition.

#### 10 Filtration And Product Recovery

The solids obtained from one of the above five processes are filtered or by other suitable methods to remove the mother liquor from the solids. The mother liquor from the separation of solid in various stages of the above purification process containing impurities. The mother liquor can be re-used repeatedly for crystallization, without any particular treatment or, if required, after being subjected to purification. The mother liquor may be recycled or purified by any suitable method, such as distillation, filtration, centrifugation, sedimentation, evaporation, cooling, adding more solvent, etc., or any combination of the methods, to separate impurities. The recovered impurities can then be recycled totally or partially to the oxidation reaction section or removed from the process.

The filtered solids may be optionally subjected to post-treatment such as washing or other methods for further removal of impurities, solvents, or acid, as described in the following section, before drying. The solids are then dried by any suitable method known to those skilled in the art to remove any residual co-solvent or traced acid and major solvents from the solids.

With one or a combination of the above mentioned processes of this invention, purified aromatic polycarboxylic acids with high purity can be obtained from the crude aromatic polycarboxylic acids.

#### Post Treatment

30 All filtered solids obtained from the above methods can be optionally washed one or more times with a co-solvent, acid solvent, or mixed solvent to remove residual impurities from the solids. The temperature of the washing solvent can be between 0



$^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , preferably from  $25^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . The amount of washing solvent used to the amount of aromatic polycarboxylic acid present is in the range from 0.01 to 100 times by molar ratio, preferably, from 0.2 to 10 times.

The particle sizes obtained from the above methods are generally finer, but more uniform, than those from the current PTA processes. As a result, the bulk density of the PTA produced by this invention may be different from those of current commercial products. If desirable, the bulk density of PTA produced by this instant invention can be adjusted by re-crystallization. This can be achieved by a number of means known to those skilled in the art. Only one example is given here. The PTA solids from this invention is dissolved in a co-solvent or acid solvent, such as water or acetic acid, at elevated temperature and pressure. The solution is then flashed under reduced process pressure or evaporated under constant or variant temperature, and with or without cooling, to produce PTA crystals that are not only similar to current commercial PTA in bulk density but also further purified to contain even less impurities.

#### 15 Synergistic Effects

It was unexpectedly found in this invention that the solubilities of impurities remained to be high in many mixed solvents with properly selected co-solvent compositions after aromatic polycarboxylic acids were precipitated out of the solution. With one or more crystallization stages, the present invention is capable to process crude aromatic polycarboxylic acids with impurity content in a range of 0.0001 to 98%, preferably from 0.5 to 30 wt%. This capability is considerably higher than the capacity of 0.5 to 1.0% of impurities that the current PTA purification processes can purify.

In addition, other impurities present in the crude aromatic polycarboxylic acids from processes other than catalytic liquid-phase oxidation process, such as DMT or NDC esterification process, can also be easily separated from the aromatic polycarboxylic acid. Therefore, this invention can be used to co-produce purified aromatic polycarboxylic acids from a new or existing aromatic polycarboxylate ester plant. For example, monomethyl terephthalate is one of the major impurity in the crude acid from DMT process, and its solubility was found to be close to the two major impurities of p-toluic acid and benzoic acid. This process can then be used to co-produce terephthalic acid from the oxidizer of a DMT plant, wherein the oxidizer

effluent is filtered or by other means to obtain the solids containing crude terephthalic acid.

Furthermore, acids used as solvent in the oxidation reaction section may be entrained with or included in the crude aromatic polycarboxylic acid. In most of  
5 current processes these residual acids need to be separated prior to entering the purification section. Since the process of this instant invention has great tolerance of residual acids presented in the crude aromatic polycarboxylic acids, residual acid recovery process steps before purification section can thus be eliminated. The present invention is capable to process crude aromatic polycarboxylic acids having residual  
10 acid solvent contents ranging from 0 to 30.0 wt%, preferably from 0 to 15 wt%, and most preferably from 0 to 5 wt%, depending on the specific aromatic polycarboxylic acid to be purified, the selected mixed solvent, and purification process conditions.

The aromatic polycarboxylic acid product purity from the present invention can be significantly higher than that obtained from the currently existing processes. Under  
15 properly selected conditions as described hereinwith, the process is even capable to remove some impurities from crude aromatic polycarboxylic acids to undetectable levels by current HPLC, High Pressure Liquid Chromatography, analytical method. As illustrated in Example 1, pure terephthalic acid with undetectable level of benzoic acid and p-toluic acid and 8 ppm of 4-CBA in a single stage of crystallization had been  
20 achieved. After optimization of the process or adding one or more crystallization stages, it is possible to reach to the purity level where all of the three impurities cannot be detected by the current HPLC measuring method. Product purity from this invention can reach to 99.99999% level. The ultra pure product can be used to develop new applications that are impossible with the current available product purity.

25 To meet polymer-grade PTA specification, current purification methods by hydrogenation or oxidation, allow total impurity level in crude terephthalic acid only up to 1 wt%, preferably 0.5 wt% to avoid overloading the purification section. To reduce impurity concentrations, either the oxidation reaction section producing crude aromatic polycarboxylic acid from starting materials is modified to run at higher  
30 severity, or additional process steps are added after the oxidation reaction step. Examples of such additional steps are secondary oxidation and reslurry in fresh acetic acid. However, since the purification process in this invention allows processing up to

98 wt% total impurity in the crude aromatic polycarboxylic acid feed and can still meet the polymer-grade specification, it relaxes requirements in the oxidation reaction section and imparts the following additional synergistic effects.

- To [a] substitute the solvent used in the crude aromatic polycarboxylic acid producing oxidation reactor with less corrosive materials, such as benzoic acid, methyl benzoate, ethyl benzoate, and phenyl benzoate, [b] use less amount of oxidation promoters, [c] use different kind of promoters, [d] reduce the severity of operating condition by reducing reaction temperature to 100 to 175 °C, [e] use a combination of the aforementioned [a] through [d] in order to use cheaper construction material, such as 316 SS, in the oxidation reactor or other parts of the process for lower capital investment.
- To run the oxidation reaction producing the crude aromatic polycarboxylic acid at a lower severity to reduce combustion loss of feedstock and acid solvent and to recycle the un-reacted feedstock back to oxidation reaction vessel to increase the overall yield and production efficiency.
- To process crude aromatic polycarboxylic acids from processes that are less efficient in producing high-purity product but cheaper in initial capital investment or operation cost. Examples are Henkel processes, HNO<sub>3</sub> oxidation of PX, the terephthalic acid or NDA from DMT or NDC process respectively, etc. Impurity contents obtained from such esterification processes may be as high as 30 wt%.

The following examples are presented hereinafter to facilitate an understanding of the process of the present invention. They are presented for the purposes of illustration only and are not intended to limit the scope of the present invention.

#### Example A (Prior Art, Comparative Example)

- A sample of CTA obtained from a PTA manufacturer with the following levels of impurities was used in the experiment:

	4-CBA	Benzoic Acid	p-Toluic Acid
PTA(ppmw)	2436	1097	515

Where ppmw means parts per million by weight.

A CTA with similar composition was then subject to a conventional hydrogenation purification method as discussed in the prior art to give a PTA product with the following impurity level:

	4-CBA	Benzoic Acid	p-Toluic Acid
PTA(ppmw)	15	0	141

5

#### Example B (Prior Art, Comparative Example)

Similar experiment as Example A is carried out with an oxidation purification process method as discussed in the prior art. The PTA product contained the following levels of impurities:

	4-CBA	Benzoic Acid	p-Toluic Acid
PTA(ppmw)	25	52	150

The impurity levels in the purified products represent typical commercially available polymer grade terephthalic acid. The following examples illustrate this instant invention.

10

#### Example 1

A sample of 15 grams of CTA used in Example A was dissolved at room temperature into a solution containing 32 grams of morpholine and 30 grams of water. The temperature of this solution was raised to and maintained at 140°C, under atmospheric pressure, long enough to reduce the total solution volume by 19ml. The solution was then cooled to allow solids to precipitate. These precipitated solids were then filtered to separate from the mother liquor. The filter cake was subsequently washed with a morpholine and water mixture. The recovered solids were then reslurried in 27 grams of acetic acid, followed by filtration, rinse with water, and drying. A dried cake, 7.4 grams, of purified terephthalic acid was obtained. Analysis with HPLC showed the PTA contained.

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20

	4-CBA	Benzoic Acid	p-Toluic Acid
PTA(ppmw)	8	0	0

#### Example 2

An experiment similar to Example 1 was carried out with a mixed solvent containing a mixture of 50% H<sub>2</sub>O and 50% N-methyl morpholine at room temperature. Terephthalic acid has negligible solubility in either pure N-methyl morpholine or water alone. Its solubility in the mixed solvent in this experiment was found to be 38 wt% at  
5 room temperature. This solution was treated with 50 wt% acetic acid in water to precipitate a crystalline terephthalic acid product of higher purity.

#### Example 3

An experiment similar to Example 2 was carried out with methanol used to replace water as the co-solvent for N-methyl morpholine. Terephthalic acid solubility was  
10 found to be 30 wt% at 60 °C. After dissolving CTA at 60 °C, the solution was allowed to cool to room temperature, at which temperature terephthalic acid has a solubility of only 8 wt%. Terephthalic acid solids with improved purity were precipitated in the process.

#### Example 4

15 An experiment similar to Experiment 2 is carried out with a mixed solvent containing 50wt% triethylamine and 50wt% water. At room temperature, terephthalic acid has negligible solubilities in either pure triethylamine or water. However, it was unexpectedly found that terephthalic acid is soluble in the mixture of triethylamine and water that contains significant portion of water. The solubility was found reaching 28  
20 wt% in the 50/50 mixture. The solubilities of benzoic acid, 4-CBA, and p-toluic acid were found to be around 155 wt%, 70 wt%, and 90 wt% in the 50/50 mixture respectively. From the above solubility data, terephthalic acid purity can be improved by first dissolving the crude terephthalic acid in a mixed solvent of 50% water and 50% triethylamine at room temperature. The water content is then reduced from  
25 50wt% to approximately 10 wt%. Terephthalic acid with improved purity can be obtained.

#### Example 5

An experiment similar to Example 4 is carried out by replacing water with methanol as the co-solvent. The solubility was found reaching to 48 wt% at room  
30 temperature in the solvent mixture which contains 50 wt% methanol. From the above solubility data, terephthalic acid purity can be improved by dissolving the crude terephthalic acid in a mixed solvent of 50 wt% methanol and 50 wt% triethylamine at

room temperature. Most of the impurities are found to remain in solution when adequate amount of acid is added to the solution to precipitate out terephthalic acid solids. When a 50 wt% of aqueous acetic acid solution is added to the solution containing CTA, terephthalic acid solids with improved purity can be obtained by precipitation.

#### Example 6

An experiment is carried out by dissolving CTA in pure N-methyl morpholine oxide at 80 °C. The solubility of terephthalic acid at 80 °C was found to be 22 wt%. However, its solubility was found to decrease to 1 wt% in a mixed solvent containing 75 wt% of water and 25wt% N-methyl morpholine oxide at room temperature. Solubilities of other impurities were found to be significantly higher than the solubility of terephthalic acid under similar conditions. The CTA containing solution is cooled down to room temperature and an amount of water equal to three times the weight of N-methyl morpholine oxide is added. Terephthalic acid of improved purity is precipitated out of the solution.

#### Example 7

An experiment similar to Example 2 is carried out to purify 2,6-naphthalene dicarboxylic acid (2,6-NDA). At room temperature 2,6-NDA has negligible solubilities in either pure morpholine or water. However, it was unexpectedly found that the solubility of 2,6-NDC increased to 12 wt% in a solvent mixture that contained 40 wt% water and 60 wt% morpholine. The solubility of 1,2,4-benzenetricarboxylic acid, a known impurity in crude 2,6-NDA, was found to be much higher at 45 wt% at 40 wt% of H<sub>2</sub>O. Solubilities of other impurities in crude 2,6-NDA are expected to be significantly higher than the solubility of 2,6-NDA.

Crude 2,6-NDA is dissolved in a mixed solvent of 40 wt% water and 60 wt% morpholine at room temperature. When a 40 wt% acetic acid in water is added to the solution containing crude 2,6-NDA, 2,6-naphthalene polycarboxylic solids with improved purity are precipitated out of the solution.

#### Example 8

An experiment similar to Example 2 is carried out to purify isophthalic acid. At room temperature a crude isophthalic acid sample is dissolved in a mixed solvent containing of 50wt% water and 50wt% morpholine. At room temperature, isophthalic

acid has negligible solubilities in either pure morpholine or water. However, in this mixed solvent containing of 50wt% water and 50wt% morpholine, the solubility of isophthalic acid was unexpectedly found to be 53 wt% at room temperature. At the same time, the solubilities of m-toluic acid and benzoic acid, known impurities in crude isophthalic acid, were found to be 50 to 105 wt% in the same mixed solvent. To this solution containing crude isophthalic acid is added acetic acid. Solids of isophthalic acid with improved purity are precipitated out of the solution.

The foregoing examples are for illustrations only, not intended to limit the scope of the present invention which is solely defined by the claims.

I claim:

1. A process for purifying a crude aromatic polycarboxylic acid having one or more condensed rings, said process comprising:

dissolving said crude aromatic polycarboxylic acid in a solvent comprising a  
5 substance selected from the group consisting of a major solvent and a mixture of a major solvent and a co-solvent wherein said co-solvent is selected from the group consisting of water, an acid solvent, an oxygen-containing solvent, and mixtures thereof, wherein the proportion of said major solvent to said co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said  
10 solvent is used in an amount from 0.1 to 100 times by weight of the amount of said crude aromatic polycarboxylic acid;

conducting a purification process; and

filtering to obtain a high purity aromatic polycarboxylic acid.

2. A process for purifying a crude aromatic polycarboxylic acid having one or three  
15 condensed rings, said process comprising:

dissolving said crude aromatic polycarboxylic acid in a solvent comprising a substance selected from the group consisting of a major solvent and a mixture of a major solvent and a co-solvents, wherein said co-solvent is selected from the group consisting of an alcohol, water, an acid solvent, an oxygen-  
20 containing solvent, and mixtures thereof, wherein the proportion of said major solvent to said co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said solvent is used in an amount from 0.1 to 100 times by weight of the amount of said crude aromatic polycarboxylic acid;

conducting a purification process; and

25 filtering to obtain a high purity aromatic polycarboxylic acid product having one or three condensed rings.

3. A process for purifying a crude aromatic polycarboxylic acid having two condensed rings, said process comprising:

dissolving said crude aromatic polycarboxylic acid in a solvent comprising a  
30 substance selected from the group consisting of an N,X-monocyclic compound and a mixture comprising an N,X-monocyclic compound and a co-solvent wherein said co-solvent is selected from the group consisting of an alcohol,



- water, an acid solvent, an oxygen-containing solvent, and mixtures thereof,  
wherein the proportion of said major solvent to said co-solvent is in the range  
of 0.1: 99.9 to 99.9:0.1 by weight, and wherein said solvent is used in an  
amount from 0.1 to 100 times by weight of the amount of said crude aromatic  
polycarboxylic acid;
- conducting a purification process to precipitate said aromatic polycarboxylic acid  
wherein the composition of said solvent is changed by removing a portion of  
said solvent; and
- filtering to obtain a high purity aromatic polycarboxylic acid product having two  
condensed rings.
4. A process for purifying a crude aromatic polycarboxylic acid having two  
condensed rings, said process comprising:
- dissolving said crude aromatic polycarboxylic acid in a solvent comprising a  
substance selected from the group consisting of an alkylamine compound and a  
mixture of an alkylamine compound and a co-solvent wherein said co-solvent is  
selected from the group consisting of an alcohol, water, acid solvent, oxygen-  
containing solvent, and mixtures thereof wherein the proportion of said major  
solvent to said co-solvent is in the range of 0.1: 99.9 to 99.9:0.1 by weight, and  
wherein said solvent is used in an amount from 0.1 to 100 times by weight of  
the amount of said crude aromatic polycarboxylic acid;
- conducting a purification process to precipitate said aromatic polycarboxylic acid  
wherein the composition of said solvent is changed by removing a portion of  
said solvent; and
- filtering to obtain a high purity aromatic polycarboxylic acid product having two  
condensed rings.
5. The process according to claim 1 or claim 2 wherein said major solvent comprises  
an N,X-monocyclic compound.
6. The process according to claim 1 or claim 2 wherein said major solvent comprises  
an alkylamine compound.
7. The process according to claim 1 or claim 2, wherein said major solvent comprises  
a mixture of an N,X-monocyclic compound and an alkylamine compound.

8. The process according to claim 3 or claim 5 wherein said N,X-monocyclic compound comprises a morpholine compound.
9. The process according to claim 1, claim 2, or claim 4 wherein said alkylamine compound is selected from the group consisting of triethylamine, triethanolamine, and mixtures thereof.
10. The process according to claim 1, wherein said major solvent comprises morpholine and said co-solvent comprises water.
11. The process according to claim 1, claim 2, claim 3, or claim 4 wherein said co-solvent comprises water.
12. The process according to claim 2, claim 3, or claim 4 wherein said co-solvent comprises an alcohol.
13. Process according to claim 12 wherein said alcohol comprises methanol.
14. The process according to claim 1, claim 2, or claim 10 wherein said aromatic polycarboxylic acid is selected from the group of terephthalic acid, isophthalic acid, phthalic acid, trimellitic acid, and pyromellitic acid.
15. The process according to claim 14 wherein said aromatic polycarboxylic acid is terephthalic acid.
16. The process according to claim 14 wherein said aromatic polycarboxylic acid is isophthalic acid.
17. The process according to claim 1, claim 3, or claim 10 wherein said aromatic polycarboxylic acid is a naphthalene dicarboxylic acid selected from the group consisting of 2,6-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, 1,7-naphthalene dicarboxylic acid, 1,8-naphthalene dicarboxylic acid, and 2,3,6-naphthalene tricarboxylic acid.
19. The process according to claim 1, 2, 3, or 4 wherein said crude aromatic carboxylic acid contains from 0.0001 wt% to 98.0wt% of impurities.
20. The process according to claim 19 wherein said crude aromatic carboxylic acid contains from 0.0001 wt% to 0.1wt% of impurities.
21. The process according to claim 19 wherein said crude aromatic carboxylic acid contains from 0.5 wt% to 30.0wt% of impurities.
22. The process according to claim 19 which further comprises recycling at least a portion of the impurities.